LEAD SOIL TREND ANALYSIS
Herculaneum Lead Smelter Site
Herculaneum, Missouri

Tetra Tech EM Inc. (Tetra Tech) was tasked by the U.S. Environmental Protection Agency (EPA) Region 7 Enforcement Fund Lead Removal program to conduct a trend analysis of soil lead concentrations at selected locations within Herculaneum, Missouri (City). Specifically, the Tetra Tech Superfund Technical Assessment and Response Team (START) 2 was requested to review and analyze data that would enable EPA to determine if soil lead concentrations were increasing over time at a variety of locations within the City. Tetra Tech was also requested to evaluate whether proximity to the smelter had any impact on whether lead concentrations were increasing. The assessment was conducted under the authority of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986. The project was assigned under START Contract No. 68-S7-01-41, Task Order No. 0027.

There are a number of sources of lead within the city – these include fugitive releases from the Doe Run Lead Smelter, tailings piles, and releases from vehicles transporting lead ore and finished lead product to and from the smelter. Doe Run Company has implemented a number improvements and procedural changes to reduce the emissions from the smelter and related operations. The last of these major changes was implemented in August 1, 2002.

One of the major concerns is whether these recently implemented activities are sufficient to ensure the properties that have been remediated to remove high levels of lead soil contamination will not be recontaminated to an unacceptable level at some future time. In order to make this determination, a number of remediated residential properties were identified for follow-up sampling and analysis. Each of the properties had contaminated soil removed and replaced with clean soil. The homes chosen for lead soil analysis varied in distance and direction from the smelter. The distance from the smelter varied from 0.20 to 1.0 miles from the smelter and the homes were north, south, and west of the smelter.
Tetra Tech focused its analysis on one data set called "Recontamination." This data set includes results from a number of locations. The data were collected from 4 different quadrants at each property and several properties also included samples from a driveway area. Lead concentrations were estimated at each location at approximately monthly intervals after the remediation was completed until September 2003 (Round 14). It should be noted that due to the sequence in which remediation occurred, not all properties had the same number of samples events; the number of events ranged from 2 to 8 events per

resident. At many locations, some intervals within the series were omitted due to weather or access restrictions. The lead concentrations were determined by use of a portable X-ray fluorescence (XRF) instrument. Samples were collected and analyzed in accordance with the quality assurance project plan (QAPP) dated September 11, 2001.

This document presents the methods used to evaluate the changes in lead soil concentrations that have occurred since each property was remediated and the results of this analysis.

Methods

Temporal and spatial trends in lead concentrations were evaluated using qualitative (graphical) and quantitative (statistical trend tests) methods. The objectives of this analysis were:

1) assess general temporal trends in lead concentrations for individual properties, and

2) evaluate spatial patterns in lead concentration as a function of the distance of individual properties from the smelter and hauling routes

Temporal trends for individual properties (Objective 1) were evaluated by first providing variability plots of lead concentrations for all sampling rounds (Figure 1). The variability plots show the individual measured concentrations for all four quadrants of each property for each sampling round. Censored or non-detect data and detected data are plotted using open and solid circles, respectively, in Figure 1. An offset vertical bar is displayed to the left of each round of data. The lower and upper horizontal lines on this bar denote the minimum and maximum reported concentrations, respectively. A third horizontal bar denotes the arithmetic mean for each round of data. The dashed horizontal line drawn across the individual plots denotes the grand arithmetic mean of the pooled data for all rounds.

Trend tests were conducted for each property using all data collected from August 1, 2002 (Round 7) to September 2003 (Round 14). A vertical dashed line and arrow in Figure 1 were used to show the starting date for conducting the trend tests. The non-parametric Mann-Kendall test was used to evaluate temporal trends for individual properties. The Mann-Kendall test is a widely used statistical test for detecting monotonic trends (that is, trends that are either increasing or decreasing) in time-series of data (Gilbert, 1987; Helsel and Hirsch, 1992; Gibbons, 1994). Because the Mann-Kendall test uses only the relative magnitude of the data rather than their measured values, it has a number of desirable properties, including, that the data do not need to be normally distributed, and that the test is not greatly affected by outliers, missing data, or censored data. Censored data are normally treated in the Mann-Kendall test by setting all non-detect values to a concentration slightly below the minimum detected concentration. However, because this analysis was conducted for pooled measurements from each of the four quadrants for each property, only the median concentrations for each sampling round were considered. Reporting limits were used for censored data in calculating the median lead concentration for each property. Each median value was effectively treated as a detected measurement for the purpose of the trend analysis. Results of the Mann-Kendall test are summarized in Figure 1. Complete details for each of the individual tests are provided in Table 1. It should be noted that a minimum of four sampling events are required to perform this test, so properties with fewer than four rounds of sampling were not evaluated.

Objective 2 was evaluated by arranging each of the plots and trend-test results for individual properties as a function of increasing distance from the smelter (Figure 1). Additionally, maps of the site can be used to identify properties that are proximate to haul routes, and this information can be also be used in a qualitative assessment of spatial patterns in lead concentration.

Results

Examination of the variability plots identified increasing trends in lead concentrations from three locations within 0.25 miles of the smelter - House Nos. 5, 20, and 22, one location within 0.45 miles - House No. 17, one location within 0.54 miles - House No. 9, and one location within 1 mile - House No. 8 (Figure 2). The monotonic trend analysis confirmed that all of the increasing trends identified through examination of the variability plots were statistically significant (Table 1). The combination of time-series plots and the results of statistical trend testing provides reasonably strong evidence that lead concentrations are increasing over time at some locations. The proportion of houses showing an increasing trend in lead concentration was greatest for properties closest to the smelter and decreased as the distance from the smelter increased.

Uncertainty

There are a number of sources of uncertainty associated with the data collected at Herculaneum and the subsequent statistical analysis that was conducted. Below are listed several sources of uncertainty and brief discussion of the potential impact on the statistical analysis.

Number of sampling events - Tetra Tech's analysis of the data from the recontamination sampling effort started with data from August 2002 (Round 7) through September 2003 (Round 14). Sampling of homes began once remediation was completed; since not all homes were remediated at the same time, the number of data points (sampling events) was not the same for all properties. Therefore, the power of the statistical trend tests and relative confidence in the test conclusions, varies for individual properties.

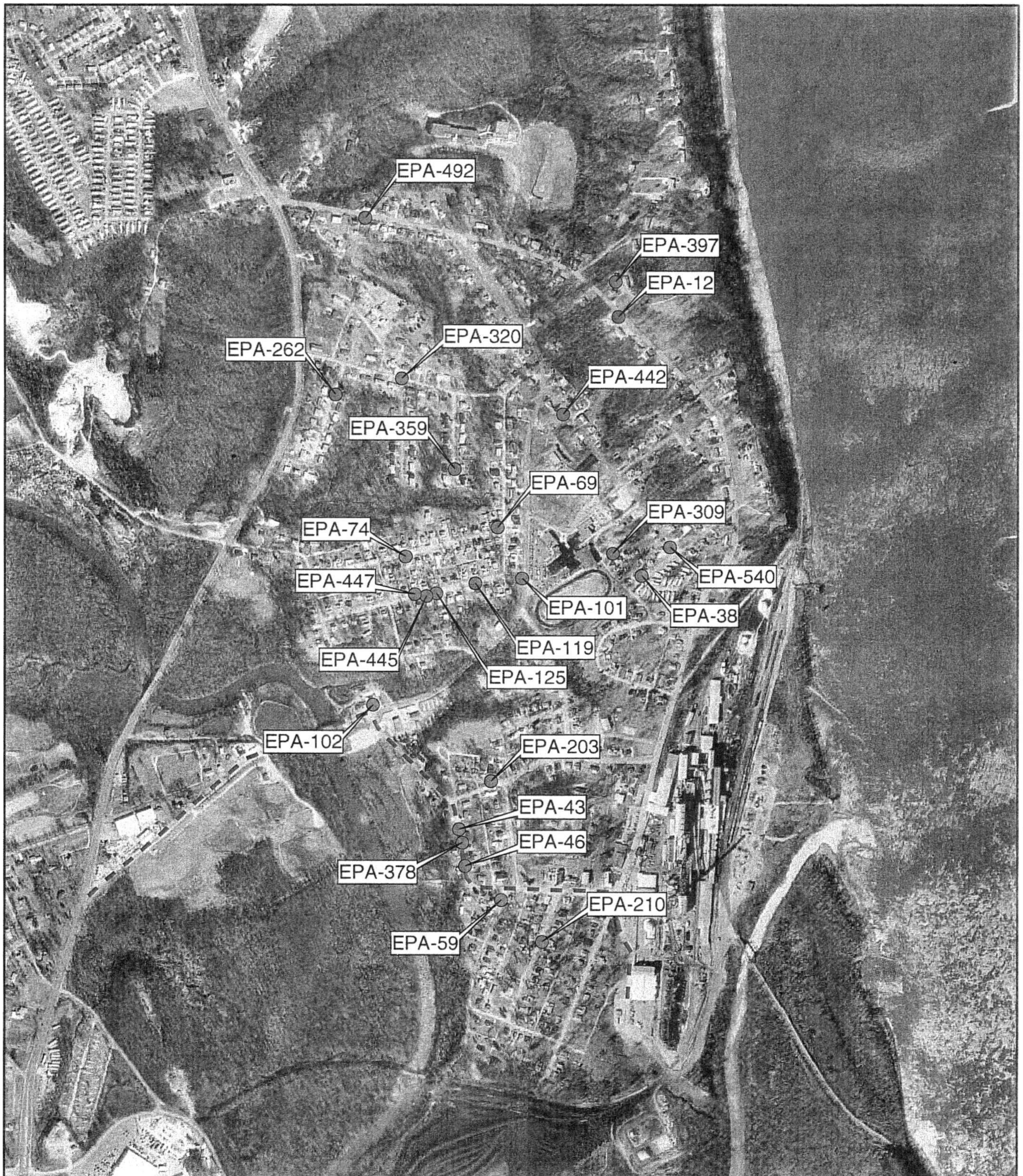
Analytical method - Lead concentrations were determined with a portable X-ray fluorescence instrument. XRF is a commonly used field-screening technique that provides rapid and reliable results for lead concentrations in soil. However, XRF measurements exhibit higher variability (lower precision) compared to conventional laboratory analysis, and this inherent variability decreases the relative magnitude of change in lead concentrations that can be detected over time. This adds to the uncertainty of the analysis, such that some changes in concentration may be occurring which can not be detected, and some changes that are observed may be a function of random error, rather than a reflection of actual increases (or decreases) in lead concentration.

REFERENCES

Gibbons, R. D. 1994. *Statistical Methods for Groundwater Monitoring*. John Wiley & Sons, Inc. New York, New York.

Gilbert, R. O. 1987. *Statistical Methods in Environmental Pollution Monitoring*. John Wiley & Sons, Inc. New York, New York.

Helsel, D. R. and R. M. Hirsh. 1992. *Statistical Methods in Water Resources*. Elsevier. New York, New York.



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Legend
- Soil Recontamination Sample
- Primary Haul Route
- Secondary Haul Route

Source: Jefferson CO., MO COQ

N

0 500 1,000
Feet

Herculaneum Lead Smelter
Herculaneum, Missouri

Figure 1
Soil Recontamination Sample Location Map

Tetra Tech Inc.

Date 12/16/03 | Drawn By: Colin Willits | Project No: G9011.L01.0027.00

TABLE

(One Page)

TABLE 1
RESULTS OF STATISTICAL TESTING FOR MONOTONIC TRENDS (MANN-KENDALL TEST) IN LEAD CONCENTRATION

Distance From Smelter	House Number	EPA Sample Number	Number of Sampling Events	Sampling Event		Test Statistic (S)	Probability > S	Trend Significant? (Yes/No)	Direction of Trend	Notes
				First	Last					
0.20	20	210	7	08/26/2002	09/23/2003	19	0.001	**Yes**	**Increasing**	
0.25	1	46	1	08/23/2002	08/23/2002	N/A	N/A	N/A	N/A	(1)
0.25	5	203	7	08/26/2002	09/23/2003	17	0.005	**Yes**	**Increasing**	
0.25	6	59	7	08/23/2002	09/23/2003	3	0.386	No	N/A	
0.25	22	378	6	08/26/2002	09/23/2003	13	0.008	**Yes**	**Increasing**	
0.25	24	43	5	11/07/2002	09/23/2003	5	0.180	No	N/A	
0.40	12	309	8	08/23/2002	09/22/2003	7	0.237	No	N/A	
0.40	13	540	7	08/23/2002	06/23/2003	3	0.386	No	N/A	
0.40	17	119	7	08/22/2002	09/23/2003	13	0.035	**Yes**	**Increasing**	
0.40	21	38	5	08/23/2002	01/15/2003	0	0.592	No	N/A	
0.45	11	101	5	08/26/2002	03/17/2003	0	0.592	No	N/A	
0.50	2	445	2	08/22/2002	09/23/2002	N/A	N/A	N/A	N/A	(1)
0.50	14	125	5	09/16/2002	06/23/2003	-2	0.408	No	N/A	
0.50	15	447	3	09/16/2002	12/09/2002	N/A	N/A	N/A	N/A	(1)
0.50	16	102	6	09/16/2002	09/23/2003	4	0.298	No	N/A	
0.50	19	69	7	08/22/2002	09/22/2003	-9	0.119	No	N/A	
0.54	9	74	7	08/22/2002	09/22/2003	15	0.015	**Yes**	**Increasing**	
0.60	4	359	6	08/22/2002	03/14/2003	2	0.430	No	N/A	
0.60	18	442	8	08/23/2002	09/22/2003	6	0.274	No	N/A	
0.75	3	12	8	08/23/2002	09/22/2003	11	0.114	No	N/A	
0.75	10	320	6	08/22/2002	03/14/2003	2	0.430	No	N/A	
0.75	23	262	4	10/08/2002	01/13/2003	3	0.271	No	N/A	
0.80	7	397	8	08/23/2002	09/23/2003	14	0.054	No	N/A	
1.00	8	492	6	08/23/2002	03/17/2003	13	0.008	**Yes**	**Increasing**	

Notes:

(1) Trend tests were not conducted with fewer than four rounds of sampling

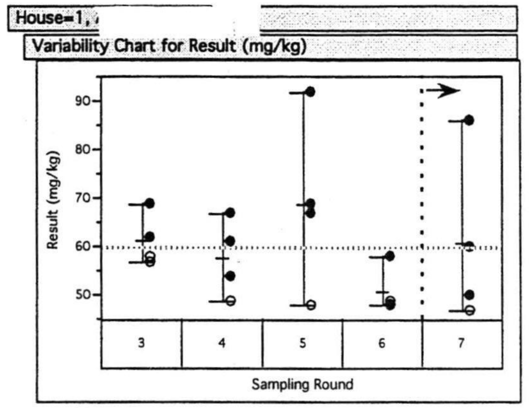
Trend testing was conducted using the median concentration for each sampling round (median of pooled quadrants)
Only samples collected after August 1, 2002 were included in the trend analysis
Monotonic trends are significant for probabilities less than or equal to 0.05
Significant negative values for the Mann-Kendall test statistic indicate that trends are decreasing
Significant positive values for the Mann-Kendall test statistic indicate that trends are increasing

FIGURE 2

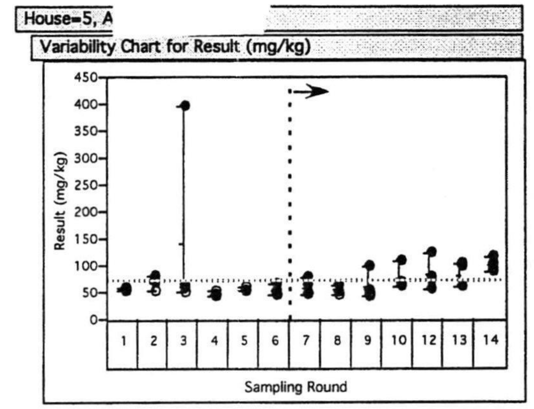
VARIABILITY PLOTS AND RESULTS OF STATISTICAL TREND TESTS FOR INDIVIDUAL PROPERTIES ORDERED BY INCREASING DISTANCE FROM THE SMELTER

Distance From Smelter (miles)

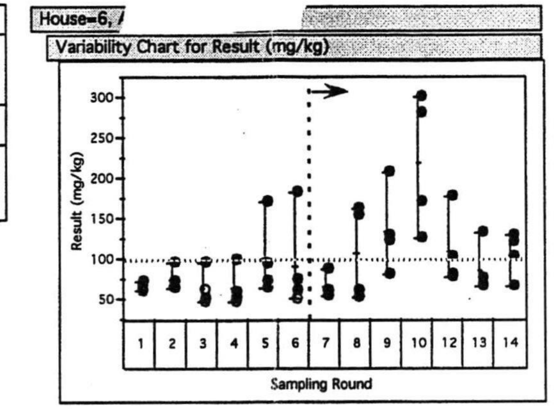
0.20-0.25



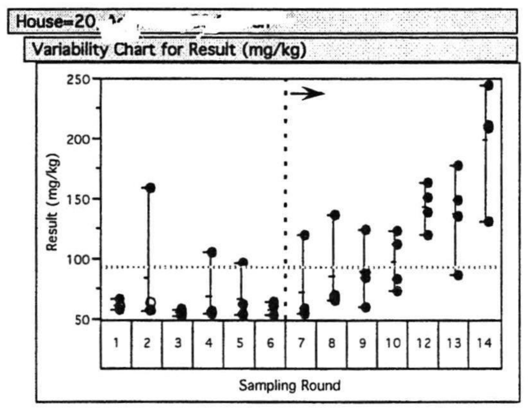
Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
1	N/A	N/A
Test Conclusion: Not Tested: n < 4		



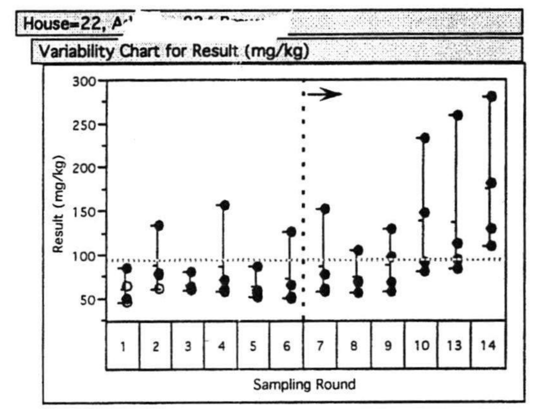
Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
7	17	0.01
Test Conclusion: Significant Increasing Trend		



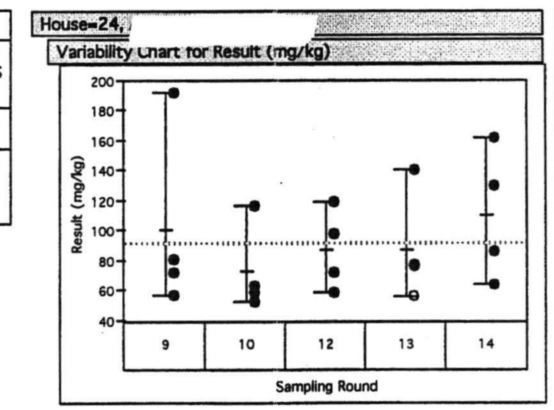
Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
7	3	0.39
Test Conclusion: No Significant Trend		



Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
7	19	<0.01
Test Conclusion: Significant Increasing Trend		

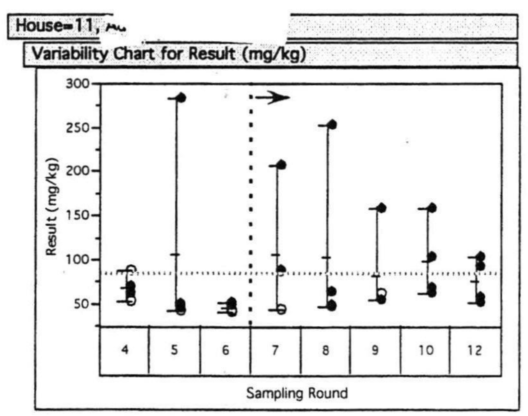


Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
6	13	0.01
Test Conclusion: Significant Increasing Trend		

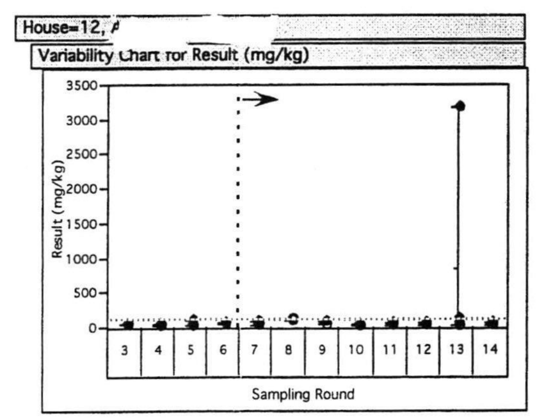


Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
5	5	0.18
Test Conclusion: No Significant Trend		

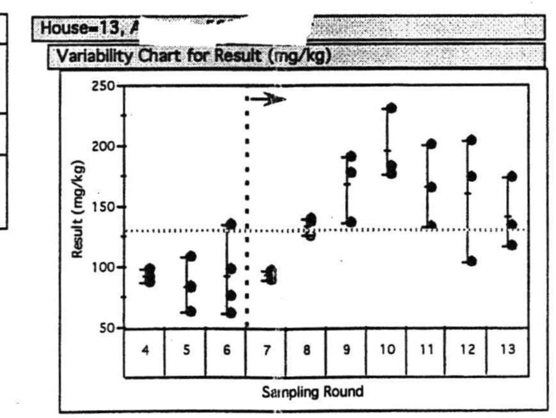
0.40-0.45



Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
5	0	0.59
Test Conclusion: No Significant Trend		



Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
8	7	0.24
Test Conclusion: No Significant Trend		



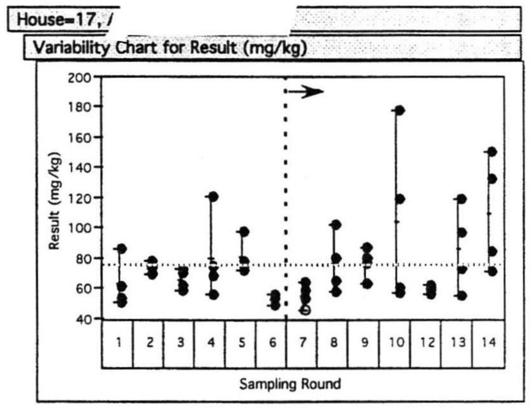
Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
7	3	0.39
Test Conclusion: No Significant Trend		

FIGURE 2 (CONTINUED)

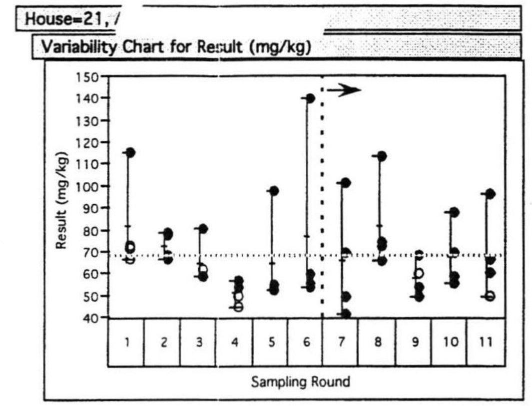
VARIABILITY PLOTS AND RESULTS OF STATISTICAL TREND TESTS FOR INDIVIDUAL PROPERTIES ORDERED BY INCREASING DISTANCE FROM THE SMELTER

Distance From Smelter (miles)

0.40-0.45

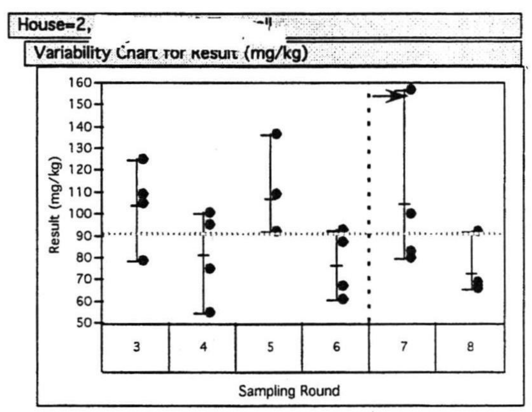


Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
7	13	0.04
Test Conclusion: Significant Increasing Trend		

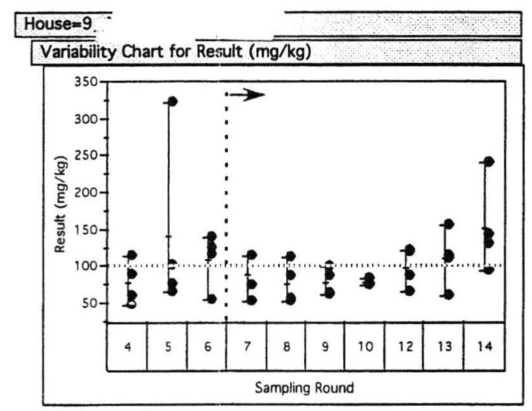


Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
5	0	0.59
Test Conclusion: No Significant Trend		

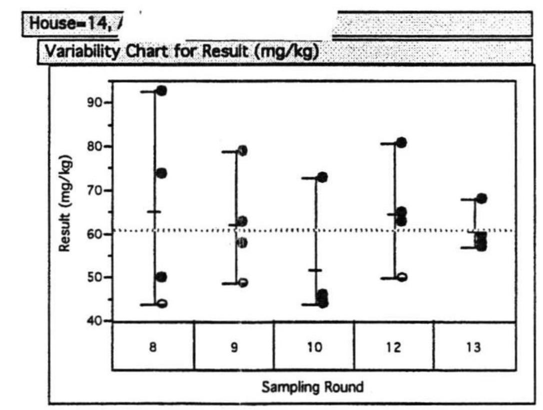
0.50-0.54



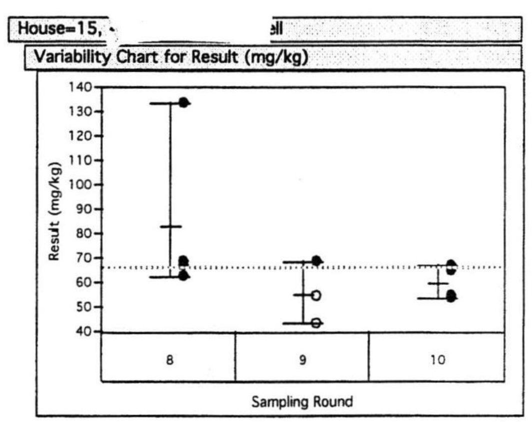
Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
2	N/A	N/A
Test Conclusion: Not Tested: n < 4		



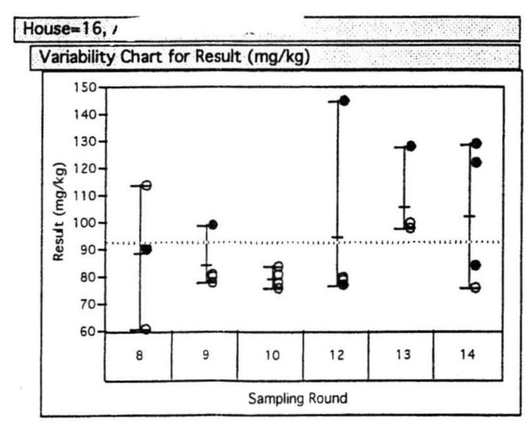
Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
7	15	0.02
Test Conclusion: Significant Increasing Trend		



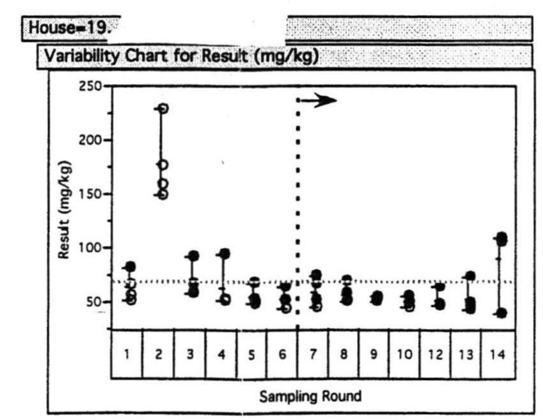
Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
5	-2	0.41
Test Conclusion: No Significant Trend		



Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
3	N/A	N/A
Test Conclusion: Not Tested: n < 4		



Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
6	4	0.30
Test Conclusion: No Significant Trend		



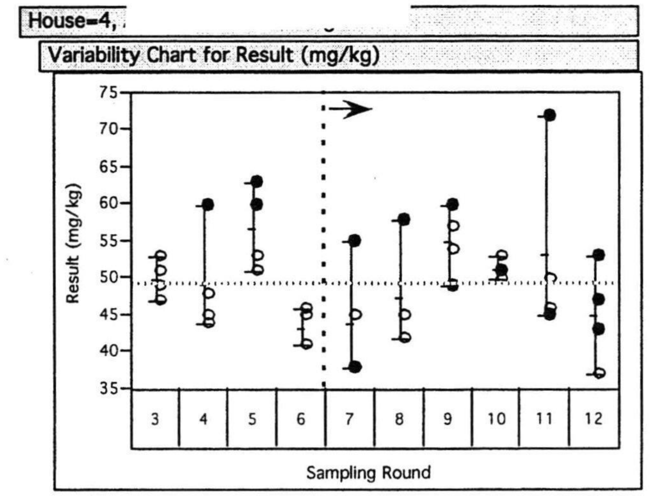
Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
7	-9	0.12
Test Conclusion: No Significant Trend		

FIGURE 2 (CONTINUED)

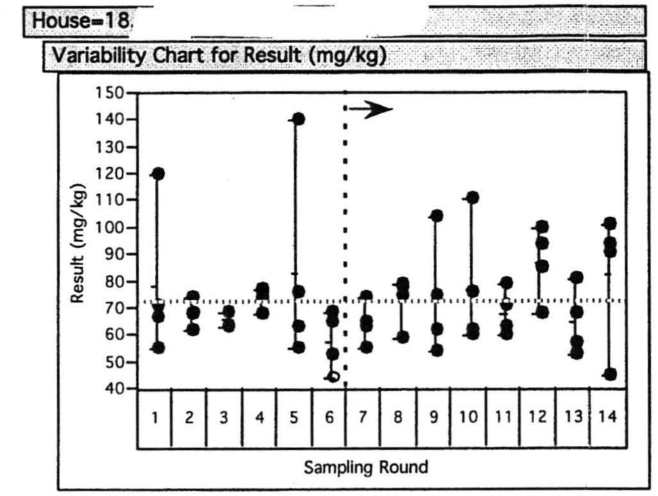
VARIABILITY PLOTS AND RESULTS OF STATISTICAL TREND TESTS FOR INDIVIDUAL PROPERTIES ORDERED BY INCREASING DISTANCE FROM THE SMELTER

Distance From Smelter (miles)

0.60

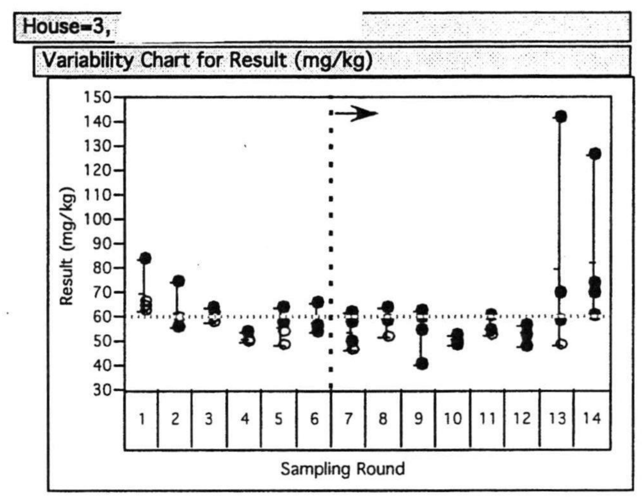


Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
6	2	0.43
Test Conclusion:		
No Significant Trend		

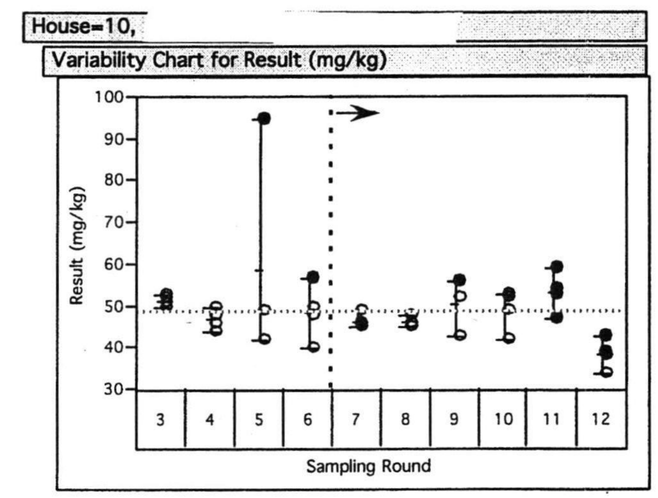


Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
8	6	0.27
Test Conclusion:		
No Significant Trend		

0.75



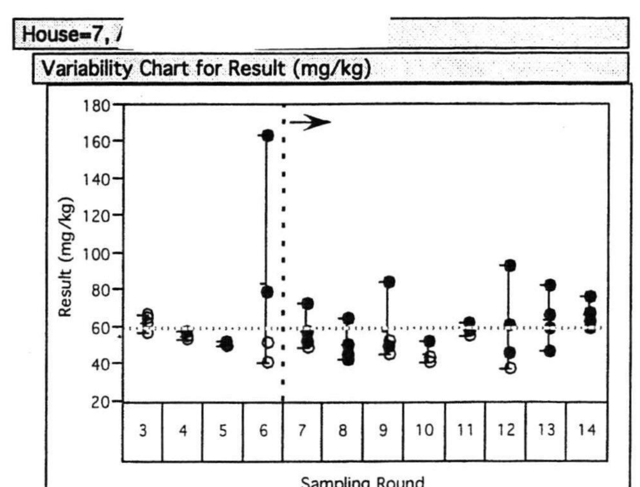
Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
8	11	0.11
Test Conclusion:		
No Significant Trend		



Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
6	2	0.43
Test Conclusion:		
No Significant Trend		

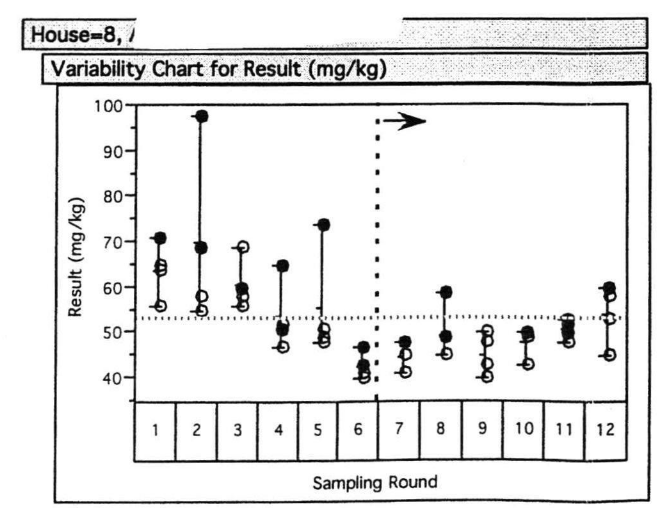
0.80-1.00

(Distance= 0.80 miles)



Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
8	14	0.054
Test Conclusion:		
No Significant Trend		

(Distance= 1.00 mile)



Mann-Kendall Trend Test		
Number of Rounds	Test Statistic (S)	Prob > S
6	13	0.01
Test Conclusion:		
Significant Increasing Trend		